Cyclization Reactions of Coordinated Alkynes in Tungsten(II) Complexes

Michael B. Wells, Peter S. White, and Joseph L. Templeton*

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received November 22, 1996[⊗]

Displacement of a CO ligand from [Tp′(CO)$_2$W{HC≡CH}][OTf] with iodide leads to the neutral parent acetylene complex Tp′(CO)(I)W{HC≡CH} (**2**). Deprotonation of **2** followed by methylation is regioselective and yields a single isomer of the propyne complex Tp′(CO)(I)W{HC≡CCH$_3$} (**3**). Deprotonation of **3** followed by alkylation with RI (R = Me, I(CH$_2$)$_n$ (n = 3−7)) is also regioselective and leads to a single isomer, Tp′(CO)(I)W{RC≡CCH$_3$} (**4**−**9**). Deprotonation of Tp′(CO)(I)W{I(CH$_2$)$_n$C≡CCH$_3$} (n = 5 (**7**), 7 (**9**)) leads to an η^2-allenyl intermediate which undergoes intramolecular alkylation (i.e. endocyclic cyclization) to form Tp′(CO)(I)W{cyclooctyne} (**10**) and Tp′(CO)(I)W{cyclodecyne} (**11**), respectively. The exocyclic cyclization precursor Tp′(CO)(I)W{PhC≡C(CH$_2$)$_5$I} (**12**) was obtained by deprotonation of the propargyl carbon of Tp′(CO)(I)W{PhC≡CCH$_3$} followed by alkylation with I(CH$_2$)$_4$I. The cyclopentyl derivative Tp′(CO)(I)W{PhC≡C(cyclopentyl)} was generated by deprotonation of **12** followed by intramolecular alkylation (i.e. exocyclic cyclization). A coordinated cyclodecyne ligand is observed in the X-ray structure of Tp′(CO)(I)W{cyclodecyne} (**11**).

Introduction

Cycloalkynes, with their synthetically versatile carbon−carbon triple bond, are important synthetic targets.[1] Strategies for alkyne synthesis normally apply to straight chains and often do not provide for cyclic analogs.[2] Several methods for cycloalkyne synthesis have been developed. However, problems with allene formation[3] and triple-bond migration[4] have hampered these methodologies. Conversion of cyclic β-keto esters to the corresponding cycloalkynes has proven useful in the synthesis of large-ring acetylenes.[5]

Cycloalkynes smaller than cyclononyne are difficult to isolate due to ring strain imposed by the acetylene unit's devotion to linearity.[1,6] Cyclooctyne has been isolated in spite of a tendency to rearrange; it is not stable in the presence of oxygen.[6b] Tetramethylcycloheptyne has also been isolated, and there is indirect evidence that the parent cycloheptyne molecule exists as a transient intermediate.[6c] Cyclohexyne has been observed spectroscopically at low temperature.[6d] Benzyne has been isolated in a matrix.[6e,f]

Krebs[6a] predicted C≡C−C angles in free cycloalkynes by assuming that the most important contribution to strain energy is angle deformation and that the angles most likely to undergo deformation are the C≡C−C angles. The bending force constant for C≡C−C angles is roughly one-third that of C−CH$_2$−C. With these constraints the C≡C−C angles calculated are 165, 155, and 140° for cyclooctyne, cycloheptyne, and cyclohexyne, respectively.

Deformation of the linear acetylene unit by more than 40° has been observed upon binding to transition metals.[7] Strained cycloalkynes are significantly stabilized by coordination to transition metals. Bennett has reported molybdenum and tungsten cyclooctyne complexes.[8] Platinum complexes of the more reactive cycloheptyne and cyclohexyne have been generated by sodium amalgam reduction of the intermediate "π-complex" formed by the reaction of the 1,2-dibromocycloalkene with Pt(PPh$_3$)$_3$.[9] These complexes were also generated by trapping the alkyne resulting from the reaction of the 1-bromocycloalkene with LDA in the presence of Pt(PPh$_3$)$_3$.[10] The reaction of 1-lithiocycloalkene (cycloalkene = cyclooctene, cycloheptene, cyclohexene) with Cp$_2$ZrMeCl followed by the addition of trimethylphosphine leads to the corresponding cycloalkyne complex Cp$_2$Zr(PMe$_3$){cycloalkyne}.[11] Organometallic

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

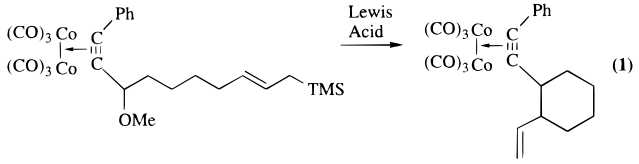
(1) Gleiter, R.; Merger, R. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995; pp 285−317.
(2) Ben-Efraim, D. A. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; pp 755−812.
(3) (a) Buchi, G.; Wuest, H. *J. Org. Chem.* **1979**, *44*, 4116. (b) Ball, W. J.; Landor, S. R. *Proc. Chem. Soc.* **1961**, 143. (c) Blomquist, A. T.; Burge, R. E.; Sucsy, A. C. *J. Am. Chem. Soc.* **1952**, *74*, 3636.
(4) Theron, F.; Verny, M.; Vessiere, R. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; pp 381−398.
(5) Boivin, J.; Huppe, S.; Zard, S. Z. *Tetrahedron Lett.* **1995**, *36*, 5737.
(6) (a) Krebs, A. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; pp 987−1062. (b) Blomquist, A. T.; Liu, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 2153. (c) Krebs, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509. (d) Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *J. Am. Chem. Soc.* **1988**, *110*, 1874. (e) Chapman, O. L.; Mattes, K.; McIntosh, C. M.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134. (f) Radziszewski, J. G.; Hess, B. A.; Zahradnik, R. *J. Am. Chem. Soc.* **1992**, *114*, 52.
(7) (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. (b) Collins, M. A.; Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 3771. (c) Feng, S. G.; Gamble, A. S.; Philipp, C. C.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504. (d) Wells, M. B.; McConathy, J. E.; White, P. S.; Templeton, J. L. Submitted for publication. (e) Melikyan, G. G.; Nicholas, K. M. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995; pp 99−132.
(8) Bennett, M. A.; Boyd, I. W. *J. Organomet. Chem.* **1985**, *290*, 165.
(9) (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1971**, *93*, 3797. (b) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (c) Bennett, M. A. *Pure Appl. Chem.* **1989**, *61*, 1695. (d) Bennett, M. A. *J. Organomet. Chem.* **1986**, *300*, 7.
(10) Lu, Z.; Abboud, K. A.; Jones, W. M. *Organometallics* **1993**, *12*, 1471.
(11) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (b) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113. (c) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441.

S0276-7333(96)00986-7 CCC: $14.00

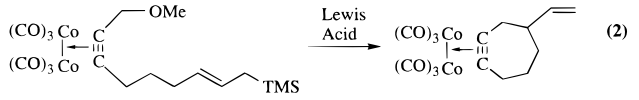
complexes of benzyne have also received attention.[11a,12]

Cycloalkyne complexes of dimers and clusters are also known. Cyclohexyne, cycloheptyne, and cyclooctyne complexes of a molybdenum dimer have been isolated from reactions with selenadiazoles.[13] Reactions between dinitriles ($N{\equiv}C(CH_2)_nC{\equiv}N$, n = 4, 5) and a tungsten dimer have resulted in dimers that contain bridging cyclohexyne and cycloheptyne.[14] Cobalt clusters with bridging cycloalkynes from cyclopentyne to cyclooctyne have been generated from the corresponding cycloalkene and $CpCo(C_2H_4)_2$.[15] Cyclopentyne has also been isolated as a three-osmium-atom cluster complex after heating $Os_3(CO)_{12}$ with cyclopentene in heptane.[16] A similar three-osmium-atom cluster complex of cyclobutyne has also been isolated from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-(phenylthio)cyclobutene.[17]

Schreiber[18] has reported both an exocyclic (eq 1) and an endocyclic (eq 2) cyclization of an alkyne bound to a cobalt carbonyl dimer. The reported chemistry is a Lewis-acid-mediated version of an intramolecular Nicholas reaction and proceeds through a propargyl cationic intermediate.[19]



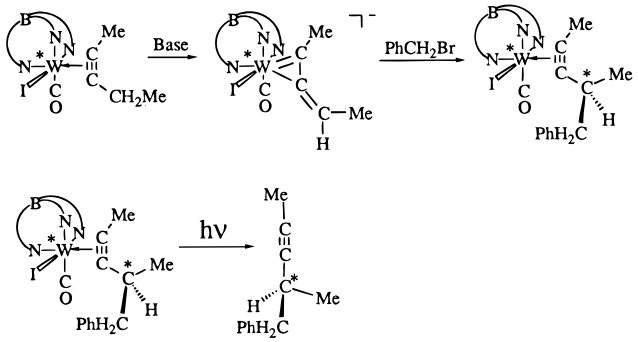
(1)



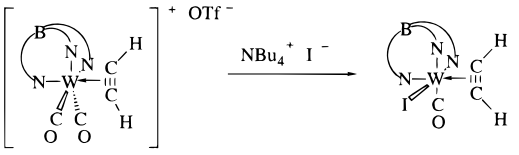
(2)

Watson and Bergman observed deuteration of the propargyl carbon site of $[Cp(CO)(Mo\{CH_3C{\equiv}CCH_3\}_2]^+$ to form $[Cp(CO)Mo\{CD_3C{\equiv}CCD_3\}_2]^+$ in acetone-d_6 solution in the presence of NEt_3.[20a] Green has generated neutral η^2-allenyl complexes by deprotonation of the cationic molybdenum complex $[Cp(P(OMe)_3)_2Mo\{PhC{\equiv}CCH_2Ph\}][BF_4]$.[20b] Deprotonation of cationic alkyne complexes of the type [(dppe)(R_2NCS_2)(CO)W{MeOC≡CCH_2Ph}][X] (dppe = $Ph_2PCH_2CH_2PPh_2$) also generates neutral η^2-allenyl complexes that add electrophiles to form the alkylated derivatives [(dppe)(R_2NCS_2)(CO) W{MeOC≡CCEHPh}][X].[20c] Stereoselective and regioselective intermolecular alkylation of the propargyl carbon of coordinated alkynes in the Tp′W(CO)(I){alkyne} system as well as a procedure to isolate the free alkyne have been developed.[7b,d] These transformations presumably proceed through an anionic η^2-allenyl intermediate (Scheme 1).

Scheme 1



Scheme 2



1 **2**

We now report the synthesis of the parent acetylene complex Tp′(CO)(I)W{HC≡CH}. Cyclization precursors have been synthesized by stepwise regioselective alkylation of the parent acetylene complex and by alkylation of the propargyl carbon of Tp′(CO)(I)W{PhC≡CCH_3}. Cyclization of these derivatives via intramolecular propargyl alkylation afforded complexes of the medium-sized cyclooctyne and cyclodecyne. Efforts to form smaller cycloalkynes were unsuccessful in spite of the bent-alkyne geometry of the reagent complexes.

Results and Discussion

Synthesis of Tp′(CO)(I)W{HC≡CH}. Facile formation of the parent acetylene complex **2** was accomplished by displacement of a carbonyl ligand from **1** with iodide (Scheme 2). The infrared and ^1H and ^{13}C NMR data are consistent with those for other four-electron-donor alkyne complexes of this type.[7] The CO stretch for **2** appears at 1896 cm^{-1} in the infrared spectrum. The ^{13}C NMR spectrum reveals a resonance at 231 ppm for the CO and resonances at 209 and 199 ppm for the acetylene carbons. Doublets at 13.6 and 12.4 ppm in the ^1H NMR spectrum with small $^3J_{HH}$ coupling (0.8 Hz) and tungsten coupling (5 Hz) have been assigned to the acetylene protons. The resonance at 12.4 ppm has been attributed to the proton *anti* to the carbonyl ligand on the basis of a comparison with the *anti* acetylenic proton resonance at 12.3 ppm for **3**, leaving the resonance at 13.6 ppm to be assigned the proton *syn* to CO (Chart 1).

Alkyne Rotational Barrier for Tp′(CO)(I)W{HC≡CH}. The acetylene rotational barrier in **2** was

(12) (a) Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163. (b) Hartwig, J. F.; Bergman, R. G.; Anderson, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404. (c) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (d) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (e) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (f) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992. (g) Fagan, P. J.; Manriques, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (h) Sarry, B.; Schaffernicht, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1238. (i) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (j) Roe, D. M.; Massey, A. G. *J. Orgamomet. Chem.* **1970**, *23*, 547. (k) Gowling, E. W.; Kettle, S. F. A.; Sharples, G. M. *Chem. Commun.* **1968**, *1*, 21.

(13) Mayr, A. J.; Carrasco-Flores, B.; Parkanyi, L.; Pannell, K. H. *J. Am. Chem. Soc.* **1992**, *114*, 5467.

(14) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Lucas, E. A. *Organometallics* **1991**, *10*, 535.

(15) Wadepohl, H.; Borchert, T.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1447.

(16) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.

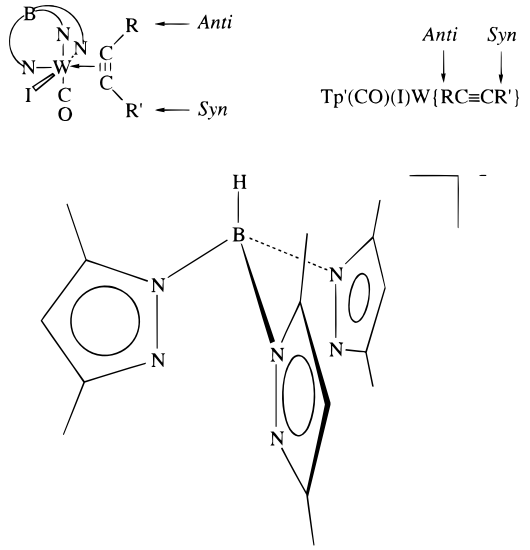
(17) Adams, R. D.; Chen, G.; Qu, X.; Wu, W.; Yamamoto, J. H. *Organometallics* **1993**, *12*, 3029.

(18) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.

(19) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207.

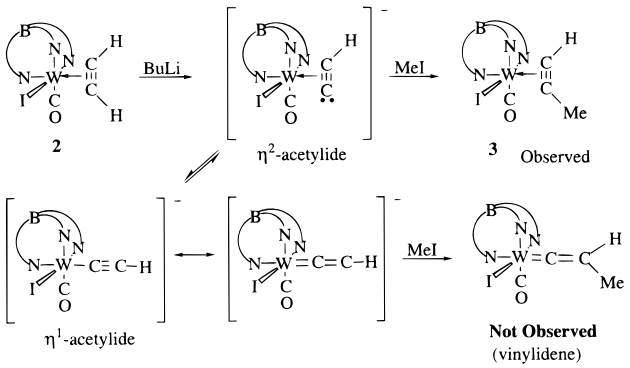
(20) (a) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698. (b) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206. (c) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818.

Chart 1. Tp′, *syn* and *anti*.



Tp' = hydridotris-(3,5-dimethylpyrazoyl)borate

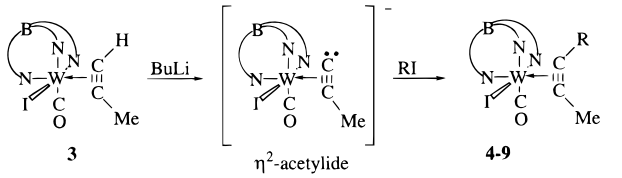
Scheme 3



calculated from line broadening in the ^{1}H NMR spectra to be 19 kcal/mol. This large barrier to alkyne rotation reflects the strong and specific π interactions among tungsten, carbonyl, and alkyne (detailed in the discussion of the X-ray structure) and is consistent with alkyne rotational barriers observed in Tp′(CO)(I)W{$CH_3C{\equiv}C(CH_2)_4I$}, Tp′(CO)(I)W{$CH_3C{\equiv}CCH_3$},[7d] Tp′(CO)(I)W{PhC≡CH}, and other d^4 alkyne complexes of the type CpMoLL′(alkyne), where L and L′ differ dramatically in their π-acidity.[7a]

Regioselective Alkylation of Tp′(CO)(I)W{HC≡CH}. Deprotonation of the green parent acetylene complex **2** generates a purple anionic intermediate which reacts with iodomethane to form a single isomer of the propyne complex **3**. The propyne methyl group resonates at 3.6 ppm in the ^{1}H NMR spectrum, typical for an alkyne methyl in the *syn* position.[7b,d] Methyl groups in the *anti* position have resonances further upfield by about 1 ppm.[7d] A single acetylenic proton signal remains at 12.3 ppm; this remaining acetylenic proton must be in the *anti* position. A likely mechanism for this methylation is removal of the *syn* proton of the bound acetylene to form an anionic η^2-acetylide intermediate, which reacts with iodomethane (Scheme 3). There is no direct evidence for the η^2-acetylide intermediate. Vinylidene formation, the probable outcome of electrophile addition to an η^1-acetylide intermediate,[21] was not observed.

Scheme 4



RI = MeI, $I(CH_2)_nI$, n =3-7

To our knowledge, there have been no reports of monomeric η^2-acetylide complexes. However, monomeric complexes that contain the isoelectronic four-electron-donor η^2-acetonitrile ligand[22a−c] and η^2-phosphaalkyne ligand[22d] have been reported. In fact, the closely related Tp′(CO)(I)W{η^2-N≡CMe} has been isolated.[22c]

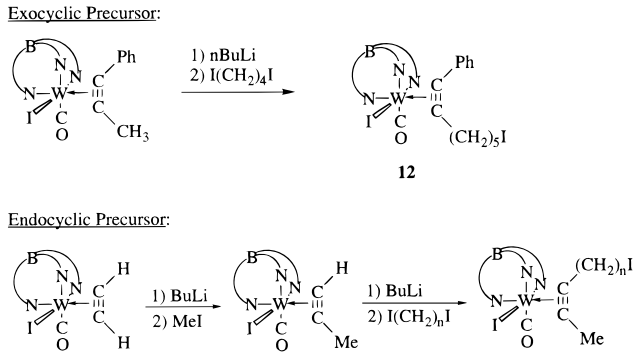
Addition of butyllithium to the propyne complex generates a dark green intermediate which reacts with alkyl halides RI (R = −Me, $-(CH_2)_nI$ (n = 3−7)) to form alkyne products: Tp′(CO)(I)W{RC≡CMe} (**4**−9) (Scheme 4). Formation of the symmetric 2-butyne complex **4** demonstrates that the *anti* acetylenic proton of **3** can be removed, even in the presence of the acidic propargyl protons, and that a second electrophile can be added. However, formation of **4** from **3** gives no definitive information about the regioselectivity of the second alkylation because of its symmetry. Conclusive information concerning the regiochemistry of the second alkylation was obtained by alkylating **3** with an electrophile other than MeI. Single isomers were obtained by alkylating **3** with $I(CH_2)_nI$. The alkyne methyl singlet in each ^{1}H NMR spectrum of these products is observed around 3.3 ppm, indicating that the methyl group remained *syn*, and thus the second electrophile added at the *anti* position. An η^2-acetylide intermediate might also be invoked here as well, since only alkyne products were obtained (Scheme 4).

Synthesis of Cyclization Precursors. The known propargyl alkylation[7b] methodology was applied in the synthesis of Tp′(CO)(I)W{PhC≡$C(CH_2)_5I$} (**12**). The *syn* methyl of Tp′(CO)(I)W{PhC≡CCH_3} was deprotonated, and $I(CH_2)_5I$ was added to the resulting anionic η^2-allenyl intermediate. Nucleophilic substitution afforded **12**. Germane ^{1}H NMR spectroscopic data include a multiplet at 3.26 ppm, integrated for two hydrogens, that has been attributed to the iodomethylene group ($-CH_2I$). A multiplet at 4.39 ppm and a multiplet at 3.70 ppm have been assigned to the diastereotopic propargyl methylene unit. The resonance for the $-CH_2I$ group is conspicuous in the ^{13}C NMR spectrum as the most upfield signal at 7.6 ppm.

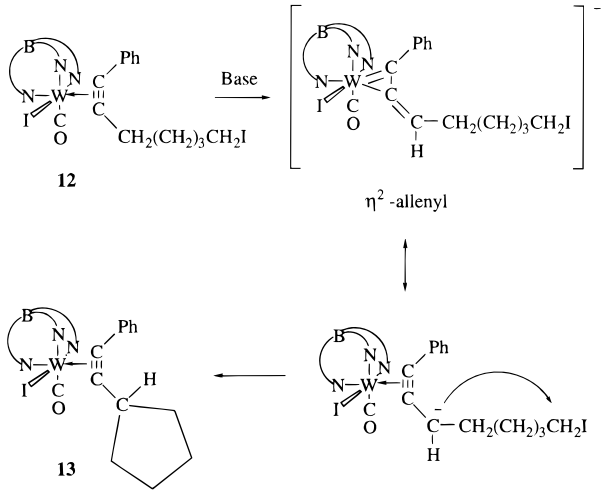
The regioselectivity of alkylation of the parent acetylene complex was utilized in the synthesis of endocyclic cyclization precursors. Single isomers of the cyclization precursors Tp′(CO)(I)W{$I(CH_2)_nC{\equiv}CCH_3$} (n = 3−7) were synthesized by alkylating the parent acetylene complex Tp′(CO)(I)W{HC≡CH} (**2**) sequentially with MeI and $I(CH_2)_nI$ (n = 3−7) (Scheme 5). This alkylation order, which places the methyl *syn* to CO and the alkyl

(21) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.
(22) (a) Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8178. (b) Barrera, J.; Sabat, M.; Harman, W. D. *Organometallics* **1993**, *12*, 4381. (c) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Organometallics* **1996**, *15*, 2428. (d) Brauers, G.; Green, M.; Jones, C.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1125.

Scheme 5. Synthesis of Cyclization Precursors



Scheme 6. Exocyclic Cyclization



iodide tail *anti* to CO, is crucial because deprotonation has been shown to occur selectively at the *syn* propargyl carbon.[7d] Attempts to cyclize complexes of the type Tp′(CO)(I)W{$CH_3C{\equiv}C(CH_2)_nI$}with the methyl in the *anti* position have not been fruitful.[23]

Several key spectroscopic features are revealed by ^1H and ^{13}C NMR spectroscopy of the cyclization precursors. As described above, each of the endocyclic precursors has a methyl resonance near 3.3 ppm indicative of its orientation *syn* to CO. A key feature of the ^1H NMR spectra of both the endocyclic and exocyclic precursors is a resonance near 3.1 ppm, which has been assigned to the diastereotopic terminal iodomethylene group ($-CH_2I$). This resonance appears as a triplet for Tp′(CO)(I)W{$CH_3C{\equiv}C(CH_2)_nI$} (**6**−**9**; $n = 4-7$). However, for the complex with the shortest alkyl iodide tail, **5** ($n = 3$), the resonance appears as a complex multiplet because the inequivalence of the protons is enhanced by proximity to the chiral metal center. The iodomethylene group resonance for Tp′(CO)(I)W{$PhC{\equiv}C(CH_2)_5I$} (**12**) also appears as a multiplet. Each iodomethylene carbon appears as a distinctive singlet near 7 ppm in the ^{13}C NMR spectra.

Exocyclic Coordination Sphere Cyclization. Addition of base (KH or KO^{t}Bu) to Tp′(CO)(I)W{$PhC{\equiv}C(CH_2)_5I$} (**12**) affords Tp′(CO)(I)W{$PhC{\equiv}C$(cyclopentyl)} (**13**) (Scheme 6). The cyclopentyl-containing complex was characterized by its ^1H and ^{13}C NMR spectra. The multiplet resonating at 3.26 ppm for the iodomethylene protons ($-CH_2I$) and one of the two multiplets assigned to a propargyl diastereotopic proton in **12** are absent in

(23) Wells, M. B.; Templeton, J. L. Unpublished results.

Scheme 7. Endocyclic Cyclization

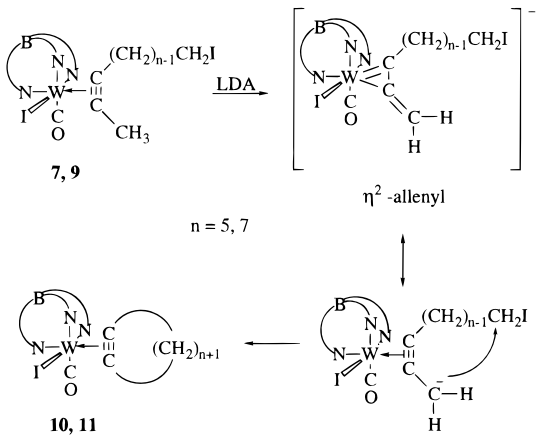


Table 1. Crystallographic Data Collection Parameters for Tp′(CO)(I)W{cyclodecyne} (11)

mol formula	$WC_{26}H_{38}N_6BOI$
fw	772.18
cryst dimens, mm	0.40 × 0.20 × 0.20
space group	$P2_1/n$
a, Å	9.6569(11)
b, Å	20.8656(13)
c, Å	14.2125(6)
β, deg	90.882(6)
V, Å^3	2863.5(4)
Z	4
calcd density, g/cm^3	1.791
radiation (wavelength, Å)	Mo Kα (0.710 73)
monochromator	graphite
linear abs coeff, mm^{-1}	5.33
scan type	*ω*
background	10% of scan width on both sides
2*θ* limits, deg	46.0
hkl ranges	−10 to +10, 0−22, 0−15
total no. of rflns	4004
no. of data with $I \geq 2.5\sigma(I)$	3250
R, %	3.9
R_w, %	4.7
GOF	1.47
no. of params	326
largest param shift/*σ*	0.004

the ^1H NMR spectrum of the product. The characteristic iodomethylene resonance at 7.6 ppm in the ^{13}C NMR spectrum of **12** is absent as well. In addition, the ^1H NMR spectrum of **13** contains a multiplet at 4.39 ppm which has been assigned to the single remaining propargyl proton. A resonance at 48.7 ppm in the ^{13}C NMR spectrum of **13** is assigned to the new tertiary propargyl carbon.

The most likely mechanism for this exocyclic ring formation is deprotonation of one of the propargyl protons, which are *syn* to CO, followed by nucleophilic ring closure of the resulting η^2-allenyl anion (Scheme 6).

Endocyclic Coordination Sphere Cyclization. Treatment of Tp′(CO)(I)W{$I(CH_2)_nC{\equiv}CCH_3$} ($n = 5$ (**7**), 7 (**9**)) with LDA produced the cycloalkyne complexes Tp′(CO)(I)W{cyclooctyne} (**10**) and Tp′(CO)(I)W{cyclodecyne} (**11**) in 69% and 44% yields, respectively, as assayed by ^1H NMR. These target cycloalkyne complexes, **10** and **11,** were also synthesized by refluxing the corresponding free cycloalkyne with Tp′$(CO)_3$(I)W. Addition of LDA to green solutions of the cyclization precursors generated a red-brown solution which slowly returned to green. This intramolecular alkylation is analogous to the intermolecular alkylation of Tp′(CO)(I)W{RC≡-

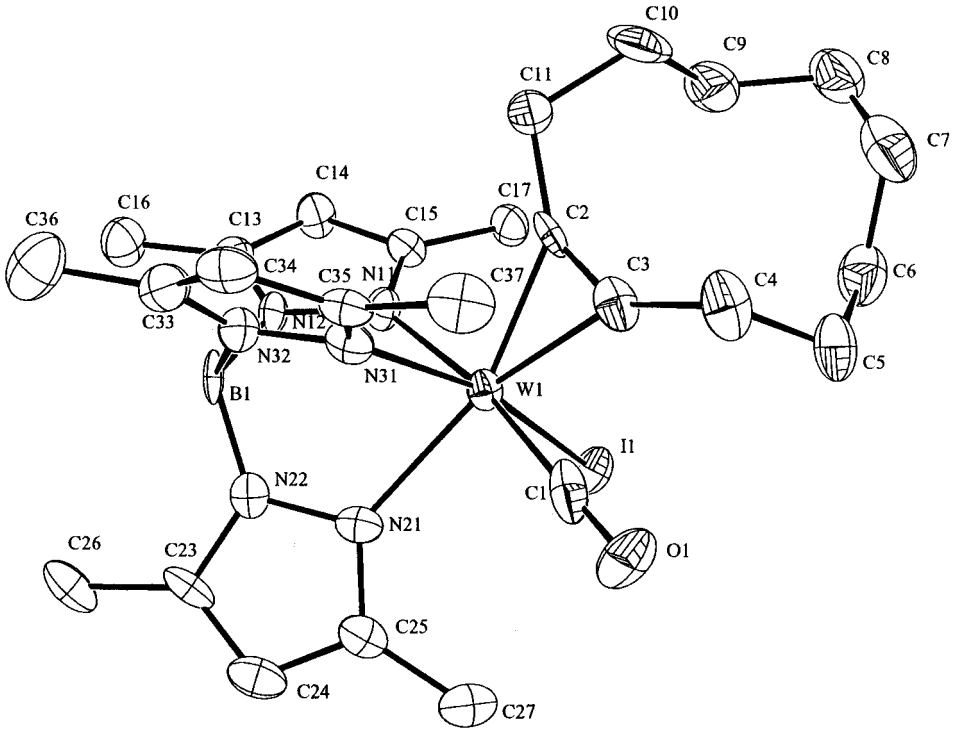


Figure 1. ORTEP drawing of Tp′(CO)(I)W{cyclodecyne} (**11**).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Tp′(CO)(I)W{cyclodecyne} (11)

W(1)−C(1)	1.91(1)	W(1)−N(31)	2.20(1)
W(1)−C(2)	2.02(1)	C(1)−O(1)	1.11(2)
W(1)−C(11)	2.06(1)	C(3)−C(4)	1.51(1)
W(1)−I(1)	2.79(1)	C(2)−C(3)	1.30(1)
W(1)−N(11)	2.25(1)	C(2)−C(11)	1.49(1)
W(1)−N(21)	2.26(1)		
C(1)−W(1)−C(2)	106.1(4)	C(3)−W(1)−N(21)	155.3(3)
C(1)−W(1)−C(3)	69.1(4)	C(3)−W(1)−N(31)	94.8(3)
C(1)−W(1)−I(1)	89.3(3)	I(1)−W(1)−N(11)	85.0(2)
C(1)−W(1)−N(11)	168.6(4)	I(1)−W(1)−N(21)	87.7(2)
C(1)−W(1)−N(21)	88.0(3)	I(1)−W(1)−N(31)	164.6(2)
C(1)−W(1)−N(31)	96.2(3)	N(11)−W(1)−N(21)	82.0(3)
C(2)−W(1)−C(3)	37.2(4)	N(11)−W(1)−N(31)	87.0(3)
C(2)−W(1)−I(1)	105.6(2)	N(21)−W(1)−N(31)	78.1(3)
C(2)−W(1)−N(11)	85.0(3)	W(1)−C(1)−O(1)	178.3(8)
C(2)−W(1)−N(21)	160.5(3)	W(1)−C(2)−C(11)	144.4(7)
C(2)−W(1)−N(31)	86.8(3)	W(1)−C(3)−C(4)	148.9(8)
C(3)−W(1)−I(1)	100.7(3)	C(3)−C(2)−C(11)	141.5(8)
C(3)−W(1)−N(11)	121.6(4)	C(2)−C(3)−C(4)	141.2(9)

CCH_2R'}.[7b,d] In these intermolecular alkylations the generation of a red-brown intermediate is indicative of η^2-allenyl anion formation. In the intramolecular alkylation a carbanion was presumably generated by selective deprotonation of the *syn* propargyl carbon. The cycloalkyne is formed when this negatively charged *syn* propargyl carbon displaces iodide from the *anti* alkyl iodide tail (Scheme 7). Attempts to cyclize the smaller precursors **5** and **6** were not successful.

X-ray Structure. An octahedral coordination sphere with the Tp′ ligand occupying three facial sites is revealed for Tp′(CO)(I)W{cyclodecyne} (**11**) by its X-ray crystal structure (Figure 1). Data collection parameters are given in Table 1. Selected bond distances and bond angles for **11** are reported in Table 2. The coordinated cyclodecyne is observed with the alkyne unit in its characteristic bent geometry, and it is oriented along the W−CO axis, as is the norm for related group VI d^4 alkyne carbonyl complexes.[7a] A molecular orbital diagram is shown in Figure 2. The filled d_{yz} orbital can donate into both the empty $\pi_{||}$* orbital of the alkyne ligand and one of the empty π* orbitals of the carbonyl. This arrangement allows the filled $\pi_{\perp}$ orbital of the alkyne to donate into the empty tungsten d_{xz} orbital. The two propargyl carbons lie approximately in the plane of the metal and the alkyne unit. The two C≡C−C angles are 141.5 and 141.2°, an average deviation from linearity for the C≡C−C unit of 39°. The remaining six-carbon aliphatic chain connects the two propargyl carbons to form a loop that passes between the Tp′ aromatic rings and out over the carbonyl ligand.

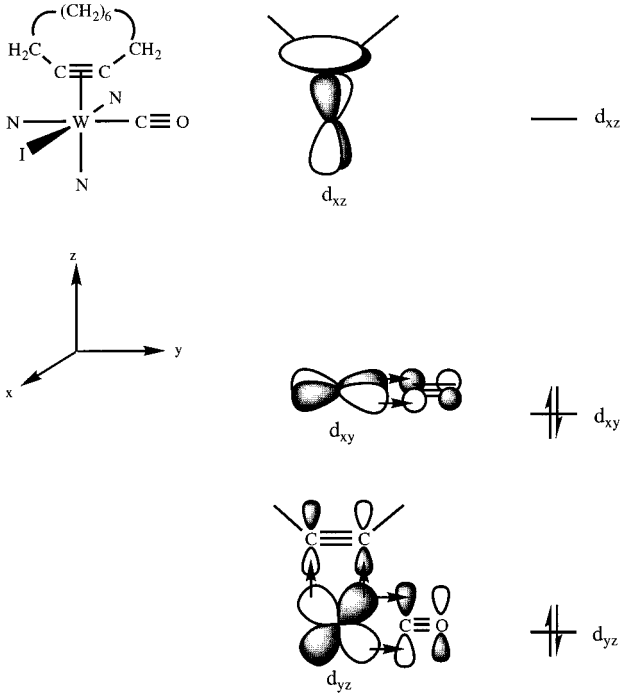


Figure 2. Molecular orbital description of Tp′(CO)(I)W{cyclodecyne} (**11**).

Summary

The parent acetylene complex Tp′(CO)(I)W{HC≡CH} was obtained by the facile displacement of a carbonyl ligand from [Tp′(CO)$_2$W{HC≡CH}][OTf] with iodide. Endocyclic cyclization precursors were formed from the parent acetylene complex by regioselective methylation followed by regioselective alkylation with I(CH$_2$)$_n$I. Cyclooctyne and cyclodecyne were formed in the coordination sphere by intramolecular propargyl alkylation of these precursors. An exocyclic cyclization precursor was generated by the intermolecular propargyl alkylation of Tp′(CO)(I)W{PhC≡CCH$_3$} with I(CH$_2$)$_4$I. Intramolecular alkylation of this precursor afforded the cyclized product Tp′(CO)(I)W{PhC≡C(cyclopentyl)}.

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), hexanes, and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from P_2O_5. Iodomethane was passed through alumina and stored over molecular sieves. All other alkyl halides were stored over molecular sieves prior to use. Butyllithium was purchased as a 2.5 M solution in hexanes from Aldrich. I(CH$_2$)$_7$I was prepared by refluxing an acetone solution of Br(CH$_2$)$_7$Br with excess NaI. Lithium diisopropylamide (LDA) was generated by addition of 1.0 equiv of butyllithium to diisopropylamine in THF solution at −78 °C. All other reagents were used as obtained from commercial sources. Tp′(CO)(I)W{PhC≡CCH$_3$},[7c] Tp′(CO)$_3$(I)W,[24] cyclooctyne, and cyclodecyne were prepared according to literature methods.[25]

Infrared spectra were collected on a Mattson Polaris FT-IR. ^{1}H and ^{13}C NMR were recorded on Varian XL 400 (400 MHz), Bruker AC 200 (200 MHz), WM250 (250 MHz), and AMX-300 (300) MHz spectrometers. Analyses were performed by Atlantic Microlab, Inc., of Norcross, GA.

[Tp′(CO)$_2$W{HC≡CH}][OTf] (1). This complex was prepared by iodide abstraction with silver triflate from Tp′(CO)$_3$W-(I) in methylene chloride at −78 °C under an acetylene atmosphere.[26]

Tp′(CO)(I)W{HC≡CH} (2). To a THF solution of tetrabutylammonium iodide (9.35 g, 25.3 mmol) was added **1** (3.00 g, 4.21 mmol). The dark green solution was stirred for 2 h. The solvent was removed, and the resulting green solid was washed with methanol. The dark green solid was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, and green crystals were grown from methylene chloride and diethyl ether (2.217 g, 3.35 mmol, 80%). IR (KBr): ν_{CO} 1896 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 13.59 (d, 1 H, $^3J_{HCCH}$ = 0.8 Hz, $^3J_{WH}$ = 5.5 Hz, *H*C≡CH); 12.42 (d, 1 H, $^3J_{HCCH}$ = 0.8 Hz, $^3J_{WH}$ = 4.5 Hz, HC≡C*H*); 6.19, 5.87, 5.73 (3 s, Tp′ C−*H*); 2.77, 2.67, 2.57, 2.40, 2.35, 1.71 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 231.3 (s, *C*O); 209.2, 198.7 (2 s, *C*≡*C*); 155.8, 155.1, 149.7, 146.5, 145.5, 144.4 (6 s, Tp′ *C*−CH$_3$); 108.7, 108.2, 107.4 (3 s, Tp′ *C*−H); 18.4, 16.5, 12.9, 12.7 (4 s (overlapping), Tp′ *C*H$_3$). Anal. Calcd for $C_{18}H_{22}N_6WBOI$: C, 32.66; H, 3.65; N, 12.70. Found: C, 32.81; H, 3.64; N, 12.69.

Tp′(CO)(I)W{HC≡CCH$_3$} (3). To a green solution of **2** (0.300 g, 0.453 mmol) in THF, cooled to −78 °C, was added butyllithium (0.27 mL, 0.68 mmol). To the resulting purple solution was added iodomethane (1.80 mL, 28.9 mmol). The color of the solution changed to green as the solution was warmed to room temperature. The solvent was removed, leaving a green oil. A ^{1}H NMR spectrum of this oil indicated the presence of a single isomer. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, and green crystals were grown from methylene chloride and hexane (0.232 g, 0.343 mmol, 76%). IR (KBr): ν_{CO} 1897 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 12.31 (s, *H*C≡CCH$_3$); 6.18, 5.89, 5.73 (3 s, Tp′ C−*H*); 3.56 (s, 3 H, HC≡CC*H*$_3$); 2.81, 2.63, 2.58, 2.42, 2.37, 1.57 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 231.7 (s, *C*O); 206.6, 205.7 (2 s, *C*≡*C*); 155.5, 155.4, 151.0, 146.6, 145.5, 144.3 (6 s, Tp′ *C*−CH$_3$); 108.6, 108.3, 107.4 (3 s, Tp′ *C*−H); 23.3, 18.4, 18.1, 16.5, 12.9, 12.8, 12.7 (7 s, Tp′ *C*H$_3$ and HC≡C*C*H$_3$). Anal. Calcd for $C_{18}H_{22}N_6WBOI$: C, 33.76; H, 3.88; N, 12.43. Found: C, 33.89; H, 3.90; N, 12.34.

Tp′(CO)(I)W{CH$_3$C≡CCH$_3$} (4).[27] To a blue-green solution of **3** (0.100 g, 0.148 mmol) in THF, cooled to −78 °C, was added butyllithium (0.089 mL, 0.22 mmol). To the resulting dark green solution was added iodomethane (0.92 mL, 1.48 mmol). The color of the solution changed to blue-green as the solution was warmed to room temperature. The solvent was removed, leaving a green oil. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, leaving a green powder (0.083 g, 0.120 mmol, 81%).

General Procedure for Synthesis of Tp′(CO)(I)W-{I(CH$_2$)$_n$C≡CCH$_3$} (n = 3−7) (5−9). Butyllithium was added to a cold THF solution (−78 °C) of **3**. Next, I(CH$_2$)$_n$I was added to this dark green solution of anion. The solution was warmed to room temperature, and then it was stirred for 1 h. The solvent was removed, and the green oil was chromatographed on alumina using a mixture of hexane and methylene chloride.

Tp′(CO)(I)W{I(CH$_2$)$_3$C≡CCH$_3$} (5). **3** (0.300 g, 0.44 mmol), butyllithium (0.21 mL, 0.53 mmol), and I(CH$_2$)$_3$I (0.26 mL, 2.2 mmol) were combined as described above. Blue-green crystals formed from methylene chloride/pentane (0.357 g, 0.42 mmol, 95%). IR (KBr): ν_{CO} 1903 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.14, 5.85, 5.72 (3 s, Tp′ C−*H*); 3.55, 2.71, 1.53 (4 m, 1:1:2 H, ICH$_2$-(C*H*$_2$)$_2$C≡CCH$_3$); 3.31 (s, 3H, −C≡CC*H*$_3$); 2.80 (m, 2H, IC*H*$_2$−); 2.82, 2.58, 2.44, 2.36, 2.33, 1.51 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 233.2 (s, *C*O); 213.5, 201.1 (2 s, *C*≡*C*); 155.4, 154.6, 150.7, 146.2, 145.5, 144.6 (6 s, Tp′ *C*−CH$_3$); 108.6, 108.2, 107.4 (3 s, Tp′ *C*−H); 36.6, 31.9, 22.2, 19.7, 18.4, 16.6, 13.0, 12.8, 12.7 (9 s, Tp′ *C*H$_3$ and ICH$_2$(*C*H$_2$)$_2$C≡*C*CH$_3$); 6.0 (s, I*C*H$_2$−). Anal. Calcd for $C_{22}H_{31}N_6WBOI_2$: C, 31.31; H, 3.70; N, 9.96. Found: C, 31.32; H, 3.65; N, 9.88.

Tp′(CO)(I)W{I(CH$_2$)$_4$C≡CCH$_3$} (6). **3** (0.300 g, 0.44 mmol) in THF, butyllithium (0.21 mL, 0.53 mmol), and I(CH$_2$)$_4$I (0.29 mL, 2.2 mmol) were combined as described above. Blue-green crystals formed from methylene chloride/pentane (0.351 g, 0.41 mmol, 92%). IR (KBr): ν_{CO} 1902 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.12, 5.84, 5.70 (3 s, Tp′ C−*H*); 3.46, 2.65, 1.47, 1.23, 1.08 (5 m, 1:1:2:1:1 H, ICH$_2$(C*H*$_2$)$_3$C≡CCH$_3$); 3.32 (s, 3H, −C≡CC*H*$_3$); 2.96 (t, 2H, $^3J_{HH}$ = 7.8 Hz, IC*H*$_2$−); 2.81, 2.57, 2.43, 2.34, 2.32, 1.51 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 233.4 (s, *C*O); 214.8, 201.1 (2 s, *C*≡*C*); 155.3, 154.4, 150.7, 146.0, 145.5, 144.5 (6 s, Tp′ *C*−CH$_3$); 108.5, 108.1, 107.3 (3 s, Tp′ *C*−H); 34.1, 33.3, 28.8, 22.3, 19.7, 18.3, 16.6, 13.0, 12.9, 12.8 (10 s, Tp′ *C*H$_3$ and ICH$_2$(*C*H$_2$)$_3$C≡*C*CH$_3$); 6.6 (s, I*C*H$_2$−). Anal. Calcd for $C_{23}H_{33}N_6WBOI_2$: C, 32.20; H, 3.88; N, 9.79. Found: C, 32.39; H, 3.93; N, 9.73.

Tp′(CO)(I)W{I(CH$_2$)$_5$C≡CCH$_3$} (7). **3** (0.250 g, 0.37 mmol) in THF, butyllithium (0.18 mL, 0.44 mmol), and I(CH$_2$)$_5$I (0.37 mL, 1.85 mmol) were combined as described above. A blue-green powder was obtained (0.295 g, 0.34 mmol, 91%). IR (KBr): ν_{CO} 1897 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.12, 5.85, 5.70 (3 s, Tp′ C−*H*); 3.43, 1.61, 1.55, 1.15, 1.00 (5 m, 1:2:1:3:1 H, ICH$_2$(C*H*$_2$)$_4$C≡CCH$_3$); 3.32 (s, 3H, −C≡CC*H*$_3$); 3.01 (t, 2H, $^3J_{HH}$

(24) Feng, S. G.; Gamble, A. S.; Philipp, C. C.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504.
(25) Lalezari, I.; Shafiee, A.; Yalpani, M. *J. Heterocycl. Chem.* **1972**, *9*, 1411.
(26) Frohnapfel, D. S.; Templeton, J. L. Unpublished results.
(27) This complex has been prepared previously by refluxing CH$_3$C≡CCH$_3$ with Tp′(CO)$_3$(I)W.[24]

= 7.8 Hz, ICH_2−); 2.83, 2.58, 2.44, 2.35, 2.34, 1.51 (6 s, 3 H each, Tp′ CH_3). ^{13}C NMR (δ, CD_2Cl_2): 233.6 (s, *C*O); 215.3, 200.9 (2 s, *C*≡*C*); 155.4, 154.5, 150.7, 146.0, 145.5, 144.5 (6 s, Tp′ *C*−CH_3); 108.5, 108.1, 107.2 (3 s, Tp′ *C*−H); 35.0, 33.4, 30.5, 26.5, 22.3, 19.6, 18.3, 16.5, 12.9, 12.8, 12.7 (11 s, Tp′ *C*H_3 and ICH$_2$(*C*H$_2$)$_4$C≡C*C*H$_3$); 6.8 (s, I*C*H$_2$−). Anal. Calcd for $C_{24}H_{35}N_6WBOI_2$: C, 33.06; H, 4.05; N, 9.64. Found: C, 33.39; H, 4.07; N, 9.56.

Tp′(CO)(I)W{I(CH$_2$)$_6$C≡CCH$_3$} (8). **3** (0.345 g, 0.51 mmol) in THF, butyllithium (0.25 mL, 0.61 mmol), and I(CH$_2$)$_6$I (0.42 mL, 2.6 mmol) were combined as described above. A blue-green powder was obtained (0.312 g, 0.35 mmol, 69%). IR (KBr): ν_{CO} 1903 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.11, 5.84, 5.70 (3 s, Tp′ C−*H*); 3.40, 1.62, 1.49, 1.20, 1.05 (5 m, 1:2:1:3:3 H, ICH$_2$(C*H*$_2$)$_5$C≡CCH$_3$); 3.31 (s, 3H, −C≡CC*H*$_3$); 3.13 (t, 2H, $^3J_{HH}$ = 7.8 Hz, IC*H*$_2$−); 2.82, 2.57, 2.42, 2.32, 2.31, 1.49 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 233.7 (s, *C*O); 215.7, 201.0 (2 s, *C*≡*C*); 155.4, 154.5, 150.7, 145.9, 145.5, 144.4 (6 s, Tp′ *C*−CH_3); 108.4, 108.1, 107.2 (3 s, Tp′ *C*−H); 35.2, 33.5, 30.4, 28.6, 27.5, 22.4, 19.6, 18.3, 16.5, 12.9, 12.8, 12.7 (12 s, Tp′ *C*H$_3$ and ICH$_2$(*C*H$_2$)$_5$C≡C*C*H$_3$); 7.5 (s, I*C*H$_2$−). Anal. Calcd for $C_{25}H_{37}N_6WBOI_2$: C, 33.89; H, 4.21; N, 9.48. Found: C, 34.89; H, 4.29; N, 9.76.

Tp′(CO)(I)W{I(CH$_2$)$_7$C≡CCH$_3$} (9). **3** (0.350 g, 0.52 mmol) in THF, butyllithium (0.25 mL, 0.61 mmol), and I(CH$_2$)$_7$I (0.911 g, 2.59 mmol) were combined as described above. A green powder was obtained (0.275 g, 0.31 mmol, 60%). IR (KBr): ν_{CO} 1903 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.10, 5.84, 5.69 (3 s, Tp′ C−*H*); 3.40, 1.74, 1.39, 1.16 (4 m, 1:2:3:6 H, ICH$_2$(C*H*$_2$)$_6$-C≡CCH$_3$); 3.30 (s, 3H, −C≡CC*H*$_3$); 3.15 (t, 2H, $^3J_{HH}$ = 7.8 Hz, IC*H*$_2$−); 2.83, 2.55, 2.42, 2.32, 2.31, 1.54 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 234.3 (s, *C*O); 212.4, 201.0 (2 s, *C*≡*C*); 155.4, 154.5, 150.8, 146.0, 145.5, 144.4 (6 s, Tp′ *C*−CH_3); 108.5, 108.1, 107.3 (3 s, Tp′ *C*−H); 34.7, 33.4, 31.2, 24.3, 22.2, 19.6, 18.6, 16.5, 12.9, 12.8, 12.7 (12 s (overlapping), Tp′ *C*H$_3$ and ICH$_2$(*C*H$_2$)$_6$C≡C*C*H$_3$); 6.8 (s, I*C*H$_2$−). Anal. Calcd for $C_{26}H_{39}N_6WBOI_2$: C, 34.69; H, 4.37; N, 9.34. Found: C, 34.91; H, 4.40; N, 9.40.

Tp′(CO)(I)W{cyclooctyne} (10). Method A. A brown solution of Tp′(CO)$_3$WI (4.03 g, 5.82 mmol) and cyclooctyne (0.703 g, 6.45 mmol) in THF was refluxed for 16 h. The solvent was removed from the resulting green solution, leaving a green oil. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, leaving a green powder (2.51 g, 3.37 mmol, 58%).

Method B. To a green solution of **7** (0.127 g, 0.145 mmol) in THF, cooled to −78 °C, was added LDA (0.174 mmol). The color of the resulting dark green solution changed to red-brown as the solution was warmed for 30 min. After the mixture was stirred at room temperature for an additional 30 min, the solvent was removed from the green solution. The resulting green oil was chromatographed on alumina, and a green band was eluted with methylene chloride. The solvent was removed, leaving a green solid (0.105 g). ^{1}H NMR revealed a 0.74:0.26 ratio of **10** to **7**, indicating that the cyclooctyne complex was formed in 69% yield. IR (KBr): ν_{CO} 1892 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.11, 5.85, 5.72 (3 s, Tp′ C−*H*); 3.55, 3.51, 3.37, 3.33, 2.05, 1.72, 1.62 (7 m, 1:1:1:1:2:3:3 H, −(C*H*$_2$)$_6$−); 2.83, 2.57, 2.44, 2.35, 2.34, 1.54 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 233.8 (s, *C*O); 215.6, 204.2 (2 s, *C*≡*C*); 155.5, 154.3, 150.2, 145.8, 145.5, 144.3 (6 s, Tp′ *C*−CH_3); 108.3, 108.1, 107.1 (3 s, Tp′ *C*−H); 38.6, 35.2, 28.1, 26.7, 26.4, 26.2, 19.6, 18.3, 16.6, 12.9, 12.8, 12.7 (12 s, Tp′ *C*H$_3$ and −(*C*H$_2$)$_6$−). Anal. Calcd for $C_{24}H_{34}N_6WBOI$: C, 38.74; H, 4.61; N, 11.29. Found: C, 38.82; H, 4.56; N, 11.23.

Tp′(CO)(I)W{cyclodecyne} (11). Method A. A brown solution of Tp′(CO)$_3$WI (1.00 g, 1.44 mmol) and cyclodecyne (0.24 g, 1.74 mmol) in THF was refluxed for 24 h. The solvent was removed from the resulting green solution, leaving a green oil. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. Green crystals were grown from methylene chloride and hexane (0.324 g, 0.42 mmol, 29%).

Method B. To a green solution of **9** (0.108 g, 0.120 mmol) in THF, cooled to −78 °C, was added LDA (0.240 mmol). The color of the resulting dark green solution changed to red-brown as the solution was warmed for 30 min. After the mixture was stirred at room temperature for an additional 2 h, the solvent was removed from the green solution. The resulting green oil was chromatographed on alumina, and a green band was eluted with methylene chloride. The solvent was removed, leaving a green solid (0.089 g). ^{1}H NMR revealed a 0.50:0.50 ratio of **11** to **9**, indicating that the cyclodecyne complex was formed in 44% yield. IR (KBr): ν_{CO} 1892 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 6.14, 5.88, 5.73 (3 s, Tp′ C−*H*); 4.73, 3.78, 3.35, 2.08, 1.85, 1.65, 1.56, 1.40, 1.00 (9 m, 1:1:1:2:4:1:1:4:1 H, −(C*H*$_2$)$_8$−); 2.89, 2.59, 2.50, 2.45, 2.36, 1.49 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 234.3 (s, *C*O); 216.7, 201.8 (2 s, *C*≡*C*); 155.5, 154.4, 149.9, 145.7, 145.4, 144.4 (6 s, Tp′ *C*−CH_3); 108.4, 108.2, 107.2 (3 s, Tp′ *C*−H); 36.3, 33.4, 25.4, 25.2, 25.1, 24.3, 22.3, 21.1, 20.3, 18.5, 16.7, 13.0, 12.9, 12.8 (14 s, Tp′ *C*H$_3$ and −(*C*H$_2$)$_8$−). Anal. Calcd for $C_{26}H_{38}N_6WBOI$: C, 40.41; H, 4.96; N, 10.88. Found: C, 40.38; H, 4.91; N, 10.94.

Tp′(CO)(I)W{PhC≡C(CH$_2$)$_5$I} (12). To a green solution of Tp′(CO)(I)W{PhC≡CCH$_3$} (1.00 g, 1.33 mmol) in THF, cooled to −78 °C, was added butyllithium (0.78 mL, 1.95 mmol). To the resulting red-brown solution was added I(CH$_2$)$_4$I (0.86 mL, 6.52 mmol). The color of the solution changed to green as the solution was warmed to room temperature. The solvent was removed, leaving a green oil. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, leaving a green powder. Green crystals were grown from methylene chloride and hexane (0.54 g, 0.58 mmol, 44%). IR (KBr): ν_{CO} 1900 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 7.22, 6.59 (2 s, 3:2 H, Ph); 5.90, 5.87, 5.72 (3 s, Tp′ C−*H*); 4.39, 3.70 (2 m, PhC≡CC*HH*(CH$_2$)$_4$I); 3.26 (m, 2 H, PhC≡CC(CH$_2$)$_4$C*H*$_2$I); 2.90, 2.60, 2.53, 2.38, 1.71, 1.37 (6 s, 3 H each, Tp′ C*H*$_3$). ^{13}C NMR (δ, CD_2Cl_2): 233.0 (s, *C*O); 209.0, 207.9 (2 s, *C*≡*C*); 155.6, 155.2, 150.1, 146.1, 145.6, 144.4, 137.9, 128.8, 128.7 (9 s, Tp′ *C*−CH_3 and Ph); 108.7, 108.3, 107.2 (3 s, Tp′ *C*−H); 36.4 (s, PhC≡C*C*H$_2$(CH$_2$)$_4$I); 33.6, 31.5, 26.8, 18.6, 18.3, 16.5, 13.0, 12.8, 12.7 (9 s, Tp′ *C*H$_3$ and PhC≡CCH$_2$(*C*H$_2$)$_3$CH$_2$I); 7.6 (s, PhC≡C(CH$_2$)$_4$*C*H$_2$I). Anal. Calcd for $C_{29}H_{37}N_6WBOI_2$: C, 37.29; H, 3.99; N, 9.00. Found: C, 37.54; H, 4.05; N, 9.04.

Tp′(CO)(I)W{PhC≡C(cyclopentyl)} (13). Method A. A green solution of **12** (2.00 g, 0.22 mmol) in THF was added to KH (0.025 g, 0.63 mmol). The mixture remained green with a white precipitate for 120 h. The solvent was removed, leaving a green oil. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, leaving a green powder. Green crystals were grown from methylene chloride and hexane (0.107 g, 0.133 mmol, 60%).

Method B. THF was added to a mixture of solid **12** (1.50 g, 0.16 mmol) and KO^{t}Bu (0.042 g, 0.37 mmol). The resulting dark green solution was stirred for 48 h. The solvent was removed, leaving a green oil. The oil was chromatographed on alumina, and a green band was eluted with a mixture of hexane and methylene chloride. The solvent was removed, leaving a green powder (0.107 g, 0.132 mmol, 81%). IR (KBr): ν_{CO} 1901 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2): 7.15, 6.47 (2 s, 3:2 H, Ph); 5.90, 5.79, 5.76 (3 s, Tp′C-*H*); 4.40 (quintet, PhC≡CC*H*CH$_2$CH$_2$CH$_2$CH$_2$); 2.89, 2.59, 2.56, 2.38, 1.67, 1.49 (6 s, 3 H each, Tp′ C*H*$_3$); 2.57, 2.35, 2.04, 1.88, 1.70 (5 m, 2:1:2:2:1 H, PhC≡CCHC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$). ^{13}C NMR (δ, CD_2Cl_2): 232.0 (s, *C*O); 211.0, 208.0 (2 s, *C*≡*C*); 155.5, 155.2, 150.1, 146.1, 145.5, 144.3, 139.0, 128.8, 128.1, 128.0 (ipso) (9 s, Tp′ *C*−CH_3 and Ph); 108.5, 108.2, 107.2 (3 s, Tp′ *C*−H); 48.7 (s, PhC≡C*C*HCH$_2$CH$_2$CH$_2$CH$_2$); 33.0, 32.1, 26.8, 26.3, 18.5, 18.4, 16.6, 13.0, 12.8, 12.7 (10 s, Tp′ *C*H$_3$ and PhC≡CCHCH$_2$CH$_2$-

$\overline{CH_2CH_2}$). Anal. Calcd for $C_{29}H_{36}N_6WBOI$: C, 43.20; H, 4.50; N, 10.42. Found: C, 43.22; H, 4.55; N, 10.35.

Variable-Temperature ^{1}H NMR Experiments. Tp′(CO)(I)W{HC≡CH} (2). A sealed-tube NMR sample of **2** in DMSO-d_6 was prepared. Spectra were recorded at 50, 70, 90, and 110 °C. Coalescence was not achieved. Line widths at half peak height ($w_{1/2}$) were measured for the acetylene proton signal at 14.5 ppm. The natural line width was subtracted from the measured line widths to give the corrected line widths ($\delta\nu$). The rate constant for site exchange (k_{ex}) was calculated from the slow-exchange approximation $k_{ex} = \pi(\delta\nu)$. The barrier to alkyne rotation ($\Delta G^{\ddagger}$) was calculated from the Eyring equation ($k_{ex} = (kT/h)\exp(-\Delta G^{\ddagger}/RT)$) at 50, 70, 90, and 110 °C to be 18.4, 18.6, 18.9, and 18.8 kcal/mol, respectively.

X-ray Structure of Tp′(CO)(I)W{cyclodecyne} (11). A green block of Tp′(CO)(I)W{cyclodecyne} of dimensions 0.40 × 0.20 × 0.20 mm was selected, mounted on a glass wand, and coated with epoxy. The crystal studied was monoclinic with space group $P2_1/n$ and unit cell dimensions a = 9.6569(11) Å, b = 20.8656(13) Å, c = 14.2125(6) Å, β = 90.882(6)°, V = 2863.5(4) Å^3, Z = 4, D_{calcd} = 1.791 g cm^{-3}, λ(Mo Kα) = 0.710 73 Å, μ = 5.22 mm^{-1}, and F(000) = 1497.17.

Diffraction data were collected on a Rigaku automated diffractometer using the ω-scan mode. Details are presented in Table 1. Of the 4004 reflections, 3250 reflections with $I > 2.5\sigma(I)$ were used in the structure solution. Final agreement indices of R = 3.9% and R_w = 4.7% resulted with hydrogens placed in calculated positions; all other atoms were refined anisotropically.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant No. CHE-9208207) for support of this research.

Supporting Information Available: Tables of thermal parameters, atomic coordinates, and all bond distances and angles for the X-ray structure of **11** (6 pages). Ordering information is given on any current masthead page.

OM960986E